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Structure and Stereochemistry of (3*R*,5*R*,8*S*,10*R*,13*R*)-*ent*-Pimara-9(11),15-dien-3-*p*-bromobenzoate (Viguiépinol)*

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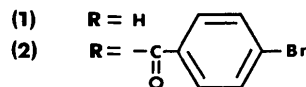
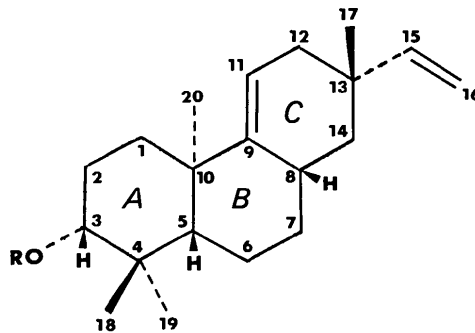
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Abstract. Systematic name: (2*R*,4*aR*,7*R*,8*aS*,10*aR*)-1-,2,3,4,5*a*,6,7,8,8*a*,9,10,10*a*-dodecahydro-1,1,4*a*,7-tetramethyl-7-vinyl-2-phenanthrenyl *p*-bromobenzoate. $C_{27}H_{35}BrO_2$, $M_r = 471.5$, orthorhombic, $P2_12_12_1$, $a = 6.220$ (2), $b = 18.773$ (7), $c = 20.708$ (7) Å, $V = 2418$ (1) Å³, $Z = 4$, $D_x = 1.29$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.70$ mm⁻¹, $F(000) = 992$, $T = 293$ K, $R = 0.063$ for 1212 observed reflections. The molecular structure and absolute configuration are determined from the X-ray data (2*a*,4*a*,7*β*,8*aβ*,10*aβ*) and confirm the structure previously assigned on the basis of chemical and spectroscopic evidence. The *A/B* and *B/C* rings are *trans* fused, with chair–twist-boat and twist-boat–half-chair conformations, respectively. The molecules in the crystal are packed at normal van der Waals distances. No unusually short intermolecular contacts are noted.

Introduction. The title compound (1) is a new diterpene which was isolated from the aerial parts of *Viguiera pinnatilobata*, a Compositae widely distributed in Mexico; the sample used was collected in Oaxaca

(Estado de Oaxaca, Mexico). Chemical and spectroscopic studies led to the proposal of the chemical structure (1) (Guerrero, Nava, Quevedo, Toscano & Soriano-García, 1985), a diterpene with an *ent*-pimarane skeleton. In order to determine unambiguously the structure and absolute configuration of (1), a *p*-bromobenzoate derivative was prepared. We have undertaken the X-ray study of this compound (2).



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Experimental. Colourless crystal $0.20 \times 0.20 \times 0.40$ mm. Nicolet R3 four-circle diffractometer. Lattice parameters from 25 machine-centred reflections with $3.9 < 2\theta < 21.2^\circ$. 1855 independent reflections with $3 < 2\theta < 45^\circ$, 1212 with $I > 2.5\sigma(I)$, index range $h 0 \rightarrow 6$, $k 0 \rightarrow 20$, $l 0 \rightarrow 22$, $R_{\text{int}} = 0.038$, ω -scan mode, variable scan speed, scan width 1.0 ($^\circ\theta$), two standard reflections (103; 004) monitored every 50 measurements, Lp correction, numerical absorption correction applied (Sheldrick, 1981); structure solved by combination of direct methods and partial structure expansion by iterative E -Fourier procedure using *SHELXTL* (Sheldrick, 1981); least-squares anisotropic refinement of all non-H atoms and H atoms riding on bonded C with fixed isotropic $U = 0.06 \text{ \AA}^2$, function minimized $\sum w(\Delta F)^2$, $w = \{\sigma^2(F_o) + G(F_o)^2\}^{-1}$, $\sigma(F_o)$ based on counting statistics, final $G = 0.001$; isotropic extinction parameter $X = 0.00007$. In the last cycle $(\Delta/\sigma)_{\text{max}} = 0.126$; $\Delta\rho -0.38$ to 0.33 e \AA^{-3} ; final $R = 0.063$, $wR = 0.062$ for the correct absolute configuration and $R = 0.074$, $wR = 0.075$ for its enantiomorph. Scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous-dispersion corrections for Br, O and C. All computations performed on a Nova 4 computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs.

Discussion. A perspective molecular drawing of (2) is shown in Fig. 1. Table 1 gives the final atomic parameters.* The bond lengths and the valence angles for non-H atoms are listed in Table 2.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and selected endocyclic torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42722 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

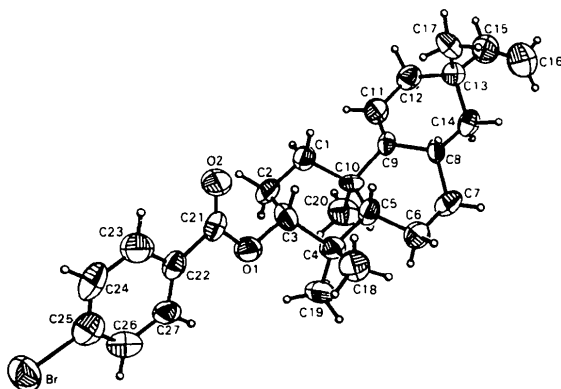


Fig. 1. The molecular conformation of (2), showing the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$$

	x	y	z	U_{eq}
Br	14615 (3)	-569 (1)	1830 (1)	89 (1)
O(1)	12069 (11)	2918 (3)	1307 (3)	55 (3)
O(2)	15091 (12)	3059 (3)	1895 (4)	82 (3)
C(1)	10287 (19)	4732 (4)	1891 (5)	52 (4)
C(2)	10486 (19)	3923 (5)	1881 (5)	56 (4)
C(3)	11721 (18)	3684 (5)	1299 (5)	54 (4)
C(4)	10771 (19)	3897 (5)	636 (5)	55 (4)
C(5)	10436 (22)	4721 (4)	669 (4)	50 (4)
C(6)	9537 (21)	5037 (5)	39 (5)	64 (4)
C(7)	8973 (19)	5831 (5)	86 (5)	60 (5)
C(8)	10169 (17)	6195 (4)	637 (4)	40 (3)
C(9)	9550 (15)	5869 (4)	1284 (4)	38 (3)
C(10)	9201 (16)	5043 (5)	1260 (5)	46 (4)
C(11)	9092 (17)	6258 (5)	1791 (5)	55 (4)
C(12)	9199 (19)	7050 (5)	1813 (5)	61 (4)
C(13)	10426 (22)	7382 (5)	1249 (5)	54 (4)
C(14)	9710 (20)	6986 (4)	630 (4)	56 (4)
C(15)	9924 (23)	8166 (6)	1235 (6)	74 (5)
C(16)	9161 (22)	8548 (6)	800 (6)	106 (6)
C(17)	12841 (20)	7313 (6)	1333 (6)	73 (5)
C(18)	12396 (18)	3730 (5)	105 (5)	69 (5)
C(19)	8684 (18)	3463 (5)	515 (5)	65 (5)
C(20)	6827 (16)	4877 (6)	1283 (5)	72 (5)
C(21)	13821 (16)	2696 (5)	1636 (4)	48 (4)
C(22)	13860 (20)	1896 (5)	1633 (5)	48 (5)
C(23)	15735 (22)	1596 (6)	1895 (6)	69 (5)
C(24)	15950 (23)	857 (7)	1941 (6)	75 (6)
C(25)	14330 (18)	436 (5)	1734 (5)	66 (4)
C(26)	12477 (21)	704 (6)	1476 (5)	59 (5)
C(27)	12320 (20)	1442 (6)	1419 (5)	55 (5)

Table 2. Bond lengths (\AA) and angles ($^\circ$), *e.s.d.*'s are given in parentheses

Br—C(25)	1.906 (10)	O(1)—C(3)	1.455 (11)
O(1)—C(21)	1.352 (12)	O(2)—C(21)	1.173 (12)
C(1)—C(2)	1.525 (12)	C(1)—C(10)	1.582 (14)
C(2)—C(3)	1.498 (15)	C(3)—C(4)	1.546 (15)
C(4)—C(5)	1.562 (12)	C(4)—C(18)	1.527 (15)
C(4)—C(19)	1.553 (15)	C(5)—C(6)	1.538 (14)
C(5)—C(10)	1.568 (14)	C(6)—C(7)	1.533 (13)
C(7)—C(8)	1.523 (13)	C(8)—C(9)	1.523 (12)
C(8)—C(14)	1.512 (11)	C(9)—C(10)	1.566 (13)
C(9)—C(11)	1.310 (13)	C(10)—C(20)	1.510 (14)
C(11)—C(12)	1.488 (13)	C(12)—C(13)	1.528 (16)
C(13)—C(14)	1.546 (14)	C(13)—C(15)	1.504 (15)
C(13)—C(17)	1.518 (18)	C(15)—C(16)	1.245 (17)
C(21)—C(22)	1.500 (14)	C(22)—C(23)	1.405 (18)
C(22)—C(27)	1.357 (16)	C(23)—C(24)	1.395 (18)
C(24)—C(25)	1.351 (17)	C(25)—C(26)	1.365 (17)
C(26)—C(27)	1.395 (16)		
C(3)—O(1)—C(21)	115.6 (7)	C(2)—C(1)—C(10)	113.1 (8)
C(1)—C(2)—C(3)	110.5 (8)	O(1)—C(3)—C(2)	111.2 (8)
O(1)—C(3)—C(4)	108.8 (7)	C(2)—C(3)—C(4)	116.1 (9)
C(3)—C(4)—C(5)	105.6 (8)	C(3)—C(4)—C(18)	109.5 (9)
C(5)—C(4)—C(18)	108.8 (8)	C(3)—C(4)—C(19)	109.1 (8)
C(5)—C(4)—C(19)	114.5 (9)	C(18)—C(4)—C(19)	109.2 (8)
C(4)—C(5)—C(6)	113.3 (8)	C(4)—C(5)—C(10)	118.8 (8)
C(6)—C(5)—C(10)	109.6 (9)	C(5)—C(6)—C(7)	113.9 (8)
C(6)—C(7)—C(8)	111.9 (8)	C(7)—C(8)—C(9)	110.7 (7)
C(7)—C(8)—C(14)	110.0 (8)	C(9)—C(8)—C(14)	110.0 (7)
C(8)—C(9)—C(10)	113.9 (7)	C(8)—C(9)—C(11)	122.4 (8)
C(10)—C(9)—C(11)	123.2 (8)	C(11)—C(10)—C(5)	107.0 (8)
C(1)—C(10)—C(9)	106.3 (7)	C(5)—C(10)—C(9)	109.8 (7)
C(1)—C(10)—C(20)	108.4 (8)	C(5)—C(10)—C(20)	115.1 (9)
C(9)—C(10)—C(20)	109.8 (8)	C(9)—C(11)—C(12)	124.9 (9)
C(11)—C(12)—C(13)	114.0 (9)	C(12)—C(13)—C(14)	107.0 (9)
C(12)—C(13)—C(15)	108.1 (9)	C(14)—C(13)—C(15)	113.3 (9)
C(12)—C(13)—C(17)	111.8 (9)	C(14)—C(13)—C(17)	109.8 (10)
C(15)—C(13)—C(17)	106.9 (10)	C(8)—C(14)—C(13)	114.2 (8)
C(13)—C(15)—C(16)	131.0 (11)	O(1)—C(21)—O(2)	126.4 (9)
O(1)—C(21)—C(22)	108.6 (8)	O(2)—C(21)—C(22)	124.9 (9)
C(21)—C(22)—C(23)	114.4 (10)	C(21)—C(22)—C(27)	128.2 (11)
C(23)—C(22)—C(27)	117.4 (10)	C(22)—C(23)—C(24)	120.4 (11)
C(23)—C(24)—C(25)	119.2 (12)	Br—C(25)—C(24)	118.5 (9)
Br—C(25)—C(26)	118.9 (8)	C(24)—C(25)—C(26)	122.5 (11)
C(25)—C(26)—C(27)	117.3 (11)	C(22)—C(27)—C(26)	123.2 (11)

The central carbon skeleton of (2) comprises a system of three *trans*-fused rings which all have tetrahedral atoms with the exception of C(9) and C(11). It is a new diterpene compound with an *ent*-pimarane skeleton and a *p*-bromobenzoate substituent at C(3).

The *A* ring is distorted from the ideal chair form because of the axial methyl–methyl interaction, C(19)⋯C(20) = 3.302 (16) Å. Rings *B* and *C* have a twist-boat and half-chair form, respectively. At the *A/B* and *B/C trans* junctions, torsion angles C(4)–C(5)–C(10)–C(1); C(6)–C(5)–C(10)–C(9) and C(7)–C(8)–C(9)–C(10); C(14)–C(8)–C(9)–C(11) are 50.9 (12); –61.8 (11)° and 37.4 (11); –12.2 (14)°, respectively.

In the *A* ring, the C(3) *p*-bromobenzoate group is in the equatorial position and the C(10) methyl group is axial. The carboxy group of the *p*-bromobenzoate substituent is oriented to minimize transannular repulsions between its O atoms and the C(4) methyl groups. The pertinent torsion angles are: C(21)–O(1)–C(3)–C(2) = –86.2 (11); C(21)–O(1)–C(3)–C(4) = 144.7 (9) and C(21)–O(1)–C(3)–H(3) = 28°, placing the C=O group *syn* to the C(3)–H bond (Mathieson, 1965; Chothia & Pauling, 1970).

The phenyl ring shows normal geometry, 1.378 (17) Å and 120.0 (11)° for the mean C(*sp*²)–C(*sp*²) bond distance and the mean internal angle. This mean bond distance is close to that given by Sutton (1965) [1.395 (5) Å] and Brisse & Sygusch (1974) (1.379 Å).

Examination of the three-dimensional packing of the molecules within the crystalline lattice (shown in Fig. 2) reveals that there are no unusually short intermolecular contacts and the molecules are packed at normal van der Waals distance.

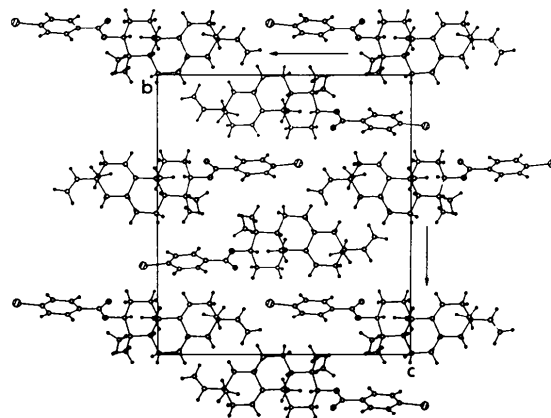


Fig. 2. The packing arrangement as viewed along *a*.

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Structure of the 1:1 Adduct Formed by *p*-Nitrophenol with Triphenylarsine Oxide

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Abstract. C₆H₅NO₃·As(C₆H₅)₃O, *M_r* = 461.35, monoclinic, *P*2₁/*n*, *a* = 8.847 (1), *b* = 15.879 (2), *c* = 15.704 (2) Å, β = 100.47 (1)°, *V* = 2169.4 (5) Å³, *Z* = 4, *D_m* = 1.390 (5) (floatation), *D_x* = 1.412 (2) g cm⁻³,

λ(Mo *K*α) = 0.71069 Å, μ = 16.86 cm⁻¹, *F*(000) = 944, room temperature. Final *R* = 0.055 for 1337 observed reflections. The adduct is formed by hydrogen bonding between the O atoms of the arsine oxide and